

MICROBially-MEDIATED SUBSURFACE CALCITE PRECIPITATION FOR REMOVAL OF HAZARDOUS DIVALENT CATIONS

Frederick S. Colwell¹, R. W. Smith², F. Grant Ferris³, Jani C. Ingram¹,
A.-L. Reysenbach⁴, Yoshiko Fujita¹, T. L. Tyler^{1,5}, J. L. Taylor^{1,5}, A. Banta⁴,
M. E. Delwiche¹, T. McLing¹, Marnie M. Cortez¹, and M. E. Watwood⁵

¹Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID 83415-2203

²University of Idaho, Idaho Falls, ID 83402

³University of Toronto, Toronto, Ontario M5S 3B1

⁴Portland State University, Portland, OR 97207-0751

⁵Idaho State University, Pocatello, ID 83209

Introduction

Radionuclide and metal contaminants are present in the vadose zone and groundwater throughout the U.S. Department of Energy (DOE) weapons complex. In situ containment and stabilization of these contaminants in vadose zones or groundwater is a cost-effective treatment strategy. However, implementing in situ containment and stabilization requires definition of the mechanism that controls contaminant sequestration. One mechanism for metals and radionuclides is co-precipitation in authigenic calcite and calcite overgrowths. Calcite, a common mineral in many aquifers and vadose zones in the arid western U.S., can incorporate divalent metals such as strontium, cadmium, lead, and cobalt into its crystal structures by the formation of solid solutions. A fundamental understanding of the coupling of calcite precipitation and trace metal partitioning and how this occurs in aquifers and vadose environments is lacking.

Our approach for encouraging calcite precipitation and co-precipitation of divalent cations relies upon addition of a carbon source to an aquifer followed by the addition of urea. Urea hydrolysis by the in situ microbial community that is starved for nitrogen causes an acceleration of calcium carbonate precipitation (and trace metal co-precipitation) by increasing groundwater pH and alkalinity. This process has been demonstrated under laboratory conditions with microorganisms that constitutively produce calcite and also with microorganisms from an aquifer of significance to DOE ¹. Because the precipitation processes are irreversible and many western aquifers are saturated with respect to calcite, the co-precipitated metals and radionuclides will be effectively removed from groundwater. The ureolysis approach has the added advantage that the ammonium ions produced by the reaction can exchange with radionuclides sorbed to subsurface minerals, thereby enhancing the susceptibility of the radionuclides for re-capture in a more stable solid phase (co-precipitation rather than adsorption). In this study our specific research objectives were to determine: 1) the treatment required to alter the aquifer microbial and geochemical conditions to enhance calcite precipitation and 2) how these treatments changed the total microbial and ureolytic communities under field conditions.

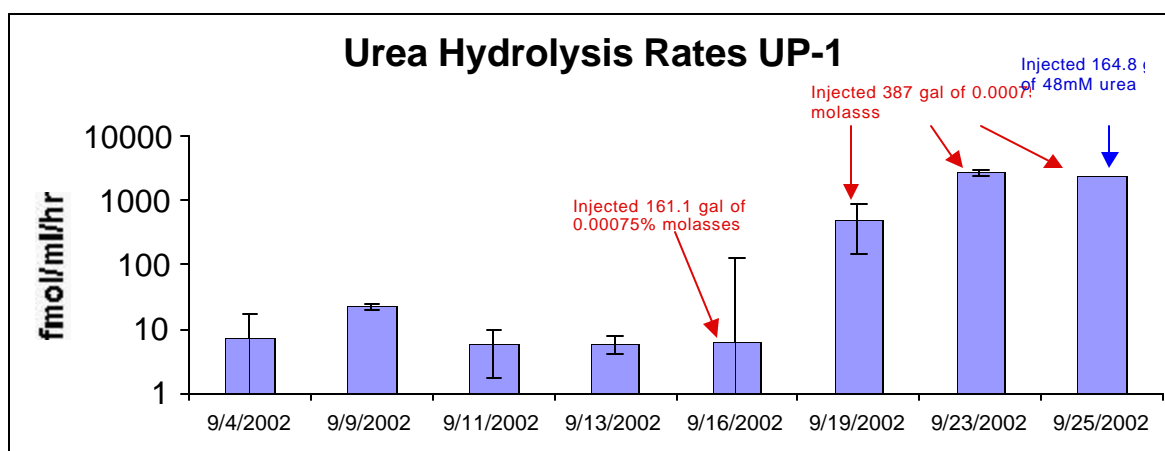
Materials and Methods

Experiments were conducted in a well (UP-1) in the Snake River Plain Aquifer (SRPA) where the depth to groundwater is 51 m. The water in UP-1 is typical of pristine locations of the SRPA (pH: 7.0; temperature: 13° C; dissolved organic carbon: 0.6 mg per L; dissolved oxygen: 7.0 mg per L). A straddle packer was used to isolate the interval between 84 and 87 m in the open borehole where the experiment would take place. Molasses (0.00075%) was added to the packed interval every three to five days on four successive occasions prior to the single addition of urea (50 mM). At four dates prior to the amendments and at each of the dates when molasses and urea were added water was collected from the well and used to determine the rate of urea hydrolysis using ^{14}C -labeled urea and the tracer method ². Water samples were also used to determine total cell numbers using acridine orange direct counts ³ and culturable heterotrophs. A precipitate recovered from the groundwater following the urea addition was characterized using x-ray diffraction analysis.

Results and Discussion

Laboratory studies indicated that bacteria in groundwater collected from the well hydrolyzed urea as rapidly as 0.6 μmole of urea per mL per day. These rates were detected in groundwater that was amended with 50 mM urea and were more than ten times higher than the values obtained when 0.5 mM urea was added to the groundwater. These rates were considerably higher than those observed during the actual field study. Urea hydrolysis rates by microbial communities taken directly from the aquifer prior to exposure to molasses was on the order of 10 fmol per mL per day (Figure 1). Following exposure of these communities to molasses urea hydrolysis rates increased by as much as 100-fold and remained high during the period leading up to the urea additions.

Figure 1



Total cell numbers in the unamended groundwater remained relatively constant and ranged from 1.5 - 1.7 x 10⁴ cells per mL on the four sampling dates leading up to the addition of molasses. These values

were in the range of total cell counts that are frequently measured in pristine locations of the SRPA ⁴. During this same period the numbers of culturable heterotrophs ranged from $0.6 - 1.2 \times 10^3$ cells per mL. Following the addition of molasses total cell numbers increased to $0.8 - 1.9 \times 10^5$ cells per mL and culturable heterotrophs increased to $0.3 - 6.7 \times 10^4$ cells per mL. After urea addition total cell numbers decreased to ca. 6.5×10^4 cells per mL with culturable heterotrophs remaining within the range measured prior to urea addition. We were unable to sample attached cells; however, our assay of free-living microorganisms indicates only a modest increase in total cell numbers due to the molasses amendments. Thus, while the addition of molasses appears to stimulate a slight increase in the total number of free-living cells (ca. 10-fold increase) it prompted a larger relative increase in the overall rates of urea hydrolysis in the same community (ca. 100-fold). It seems likely that a higher fraction of the total cells were urease positive after the molasses additions than before the additions.

Following urea addition water that was pumped from the well contained a white precipitate that was not evident in any of the samples of the unamended or molasses amended aquifer. X-ray diffraction analysis of this precipitate indicated that the material was composed predominantly of calcite.

The results from this field experiment in a pristine location in the Snake River Plain aquifer involving the phased addition of molasses and then urea showed increases in total cell numbers, the rate of community urea hydrolysis, and calcite formation over the course of the study. Subsurface remediation of divalent cations (e.g., ⁹⁰Sr) using this biogeochemical manipulation would appear to be promising for arid western DOE sites such as Hanford and the Idaho National Engineering and Environmental Laboratory.

References

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